ENERGY earthshots U.S. DEPARTMENT OF ENERGY | Hydrogen

# Waste to Biohydrogen via Fermentation

Pin-Ching Maness, National Renewable Energy Laboratory

Hydrogen Shot Summit

# Waste to BioHydrogen

## Feedstock

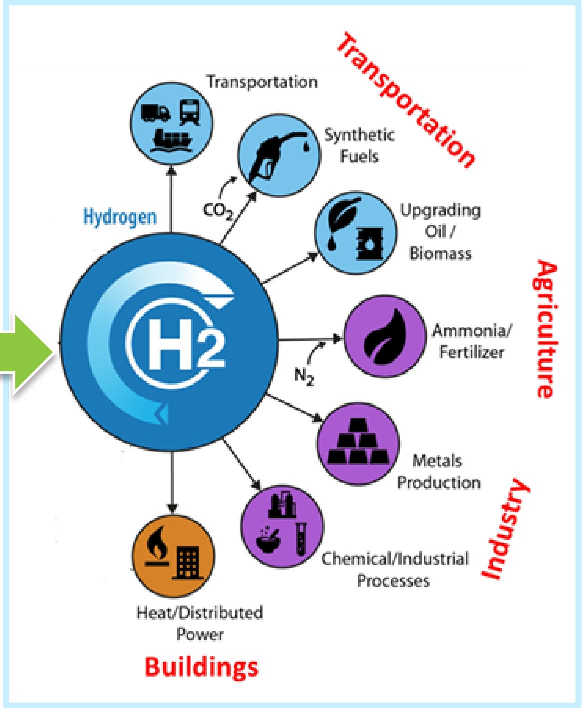
Agricultural Waste

Forest Residue

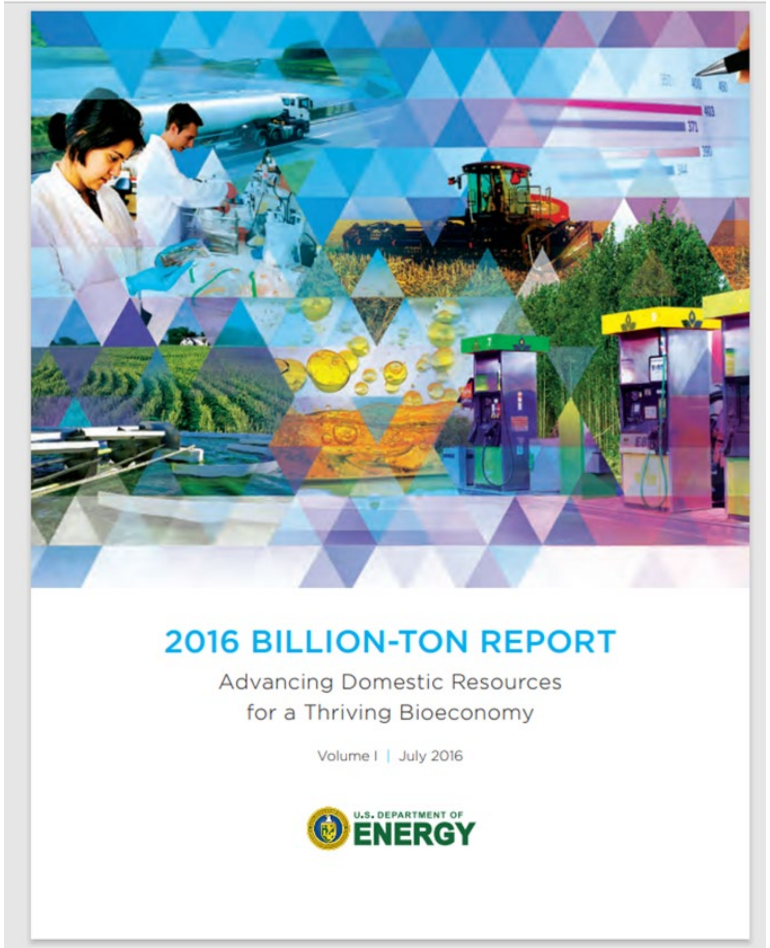

Aqueous Waste

## Fermentation

Microbial Catalysts for $H_2$ Production

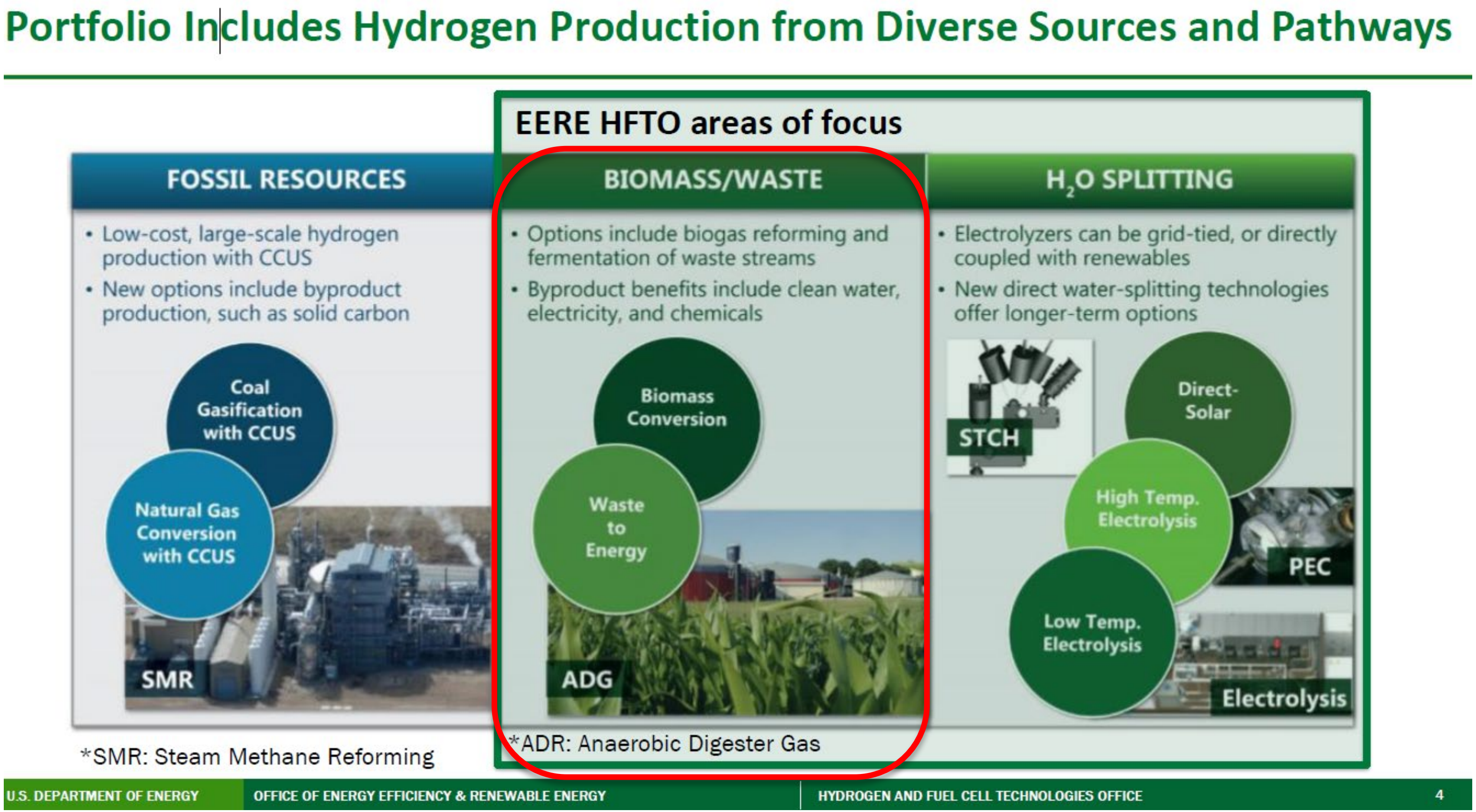


# Why Biohydrogen




- **Renewable** – convert waste to renewable $H_2$: monetize waste and its removal
- **Scalable**
  - DOE-USDA **Billion-Ton Report** estimated one billion tons of waste biomass is available for fuels and chemicals, i.e.,$H_2$
  - Bioreactors is a mature technology
- **Continuous Productivity** in the dark
- **Microbial Catalysis** – many microbes naturally can produce $H_2$ without using the expensive precious metals.

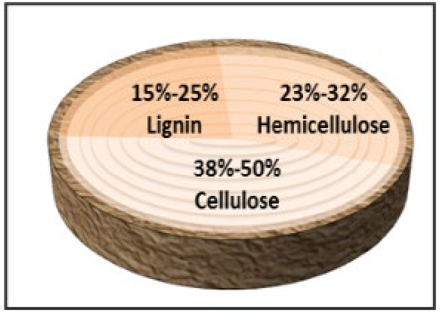
# Relevance to US DOE HFTO and Hydrogen Shot

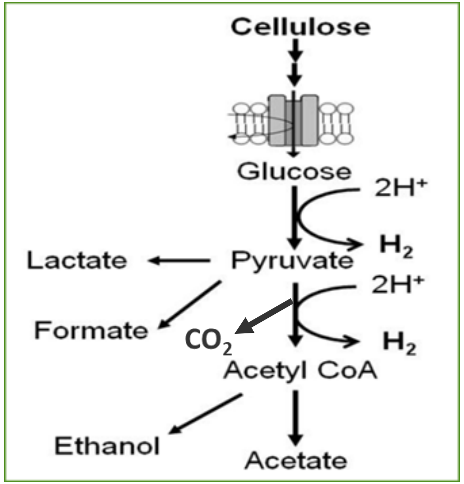



*Sourced from March 11, 2021, Sustainable Energy Council (SEC) World Hydrogen Summit by Dr. Sunita Satyapal

# Technical Challenges and Approaches

- Lignocellulosic biomass has three polymers: cellulose (six-carbon glucose), hemicellulose (five-carbon xylose), and lignin.
- $H_2$ yield via fermentation is low: 4 mol $H_2$/mol sugar if <u>only acetate</u> produced.
- In practice, fermentation effluent contains other compounds (alcohols and organic acids).

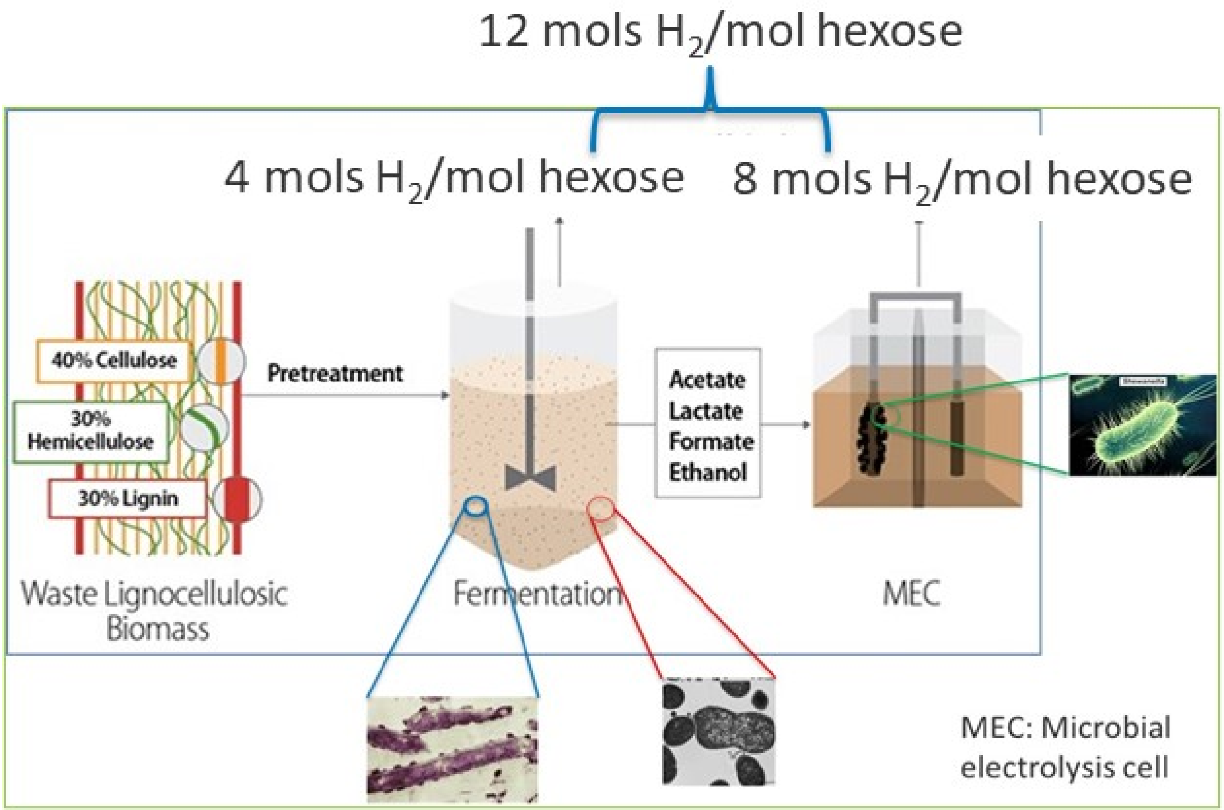



| Challenges | Approaches |
|---|---|
| **Feedstock Cost** | •Use microbe that can **<u>directly</u>** convert cellulose to $H_2$<br>• Engineer cellulosic microbe to co-utilize hemicellulose |
| **$H_2$ Molar Yield (mol $H_2$/mol sugar)** | •Metabolic engineering to redirect pathways toward more $H_2$<br>•Integrate fermentation with MEC* to increase $H_2$ yield and remove waste. |

*MEC: Microbial electrolysis cell

# Integrating Fermentation with Microbial Electrolysis Cell




Lalaurette et al. (2009) *Intl. J. Hydrogen Energy*

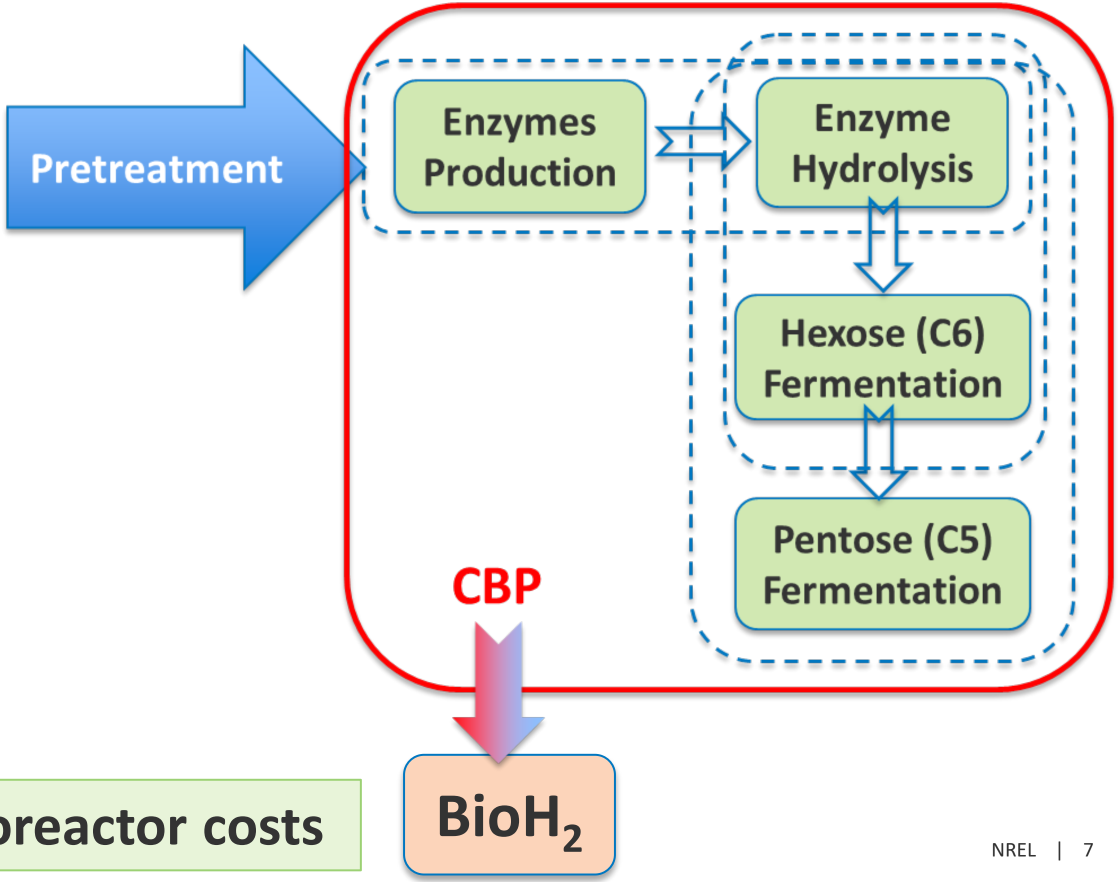
A NREL-Penn State integrated system has reported a **combined $H_2$ molar yield >10.**

Bruce Logan of Penn State Univ. will elaborate MEC.

# *Clostridium thermocellum* – the Microbe of Choice

- A fast cellulose-degrader, at 55-60 $^{o}C$
- A good $H_2$ producer
- *C. thermocellum* can
  - generate its own enzyme cocktails
  - hydrolyze cellulose
  - ferment
- Consolidated BioProcessing (CBP)

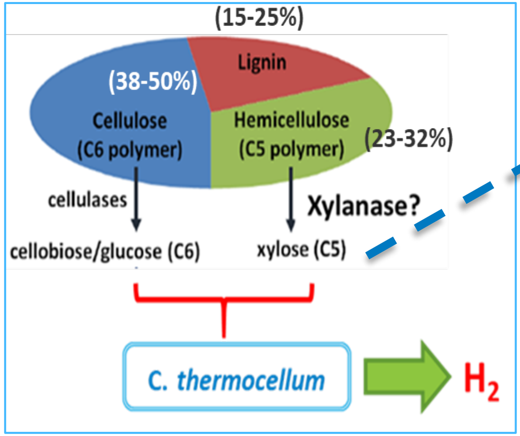
Corn Stover




**CBP lowers feedstock and bioreactor costs**

# Breakthrough Achievements to Utilize Hemicellulose

- Yet *C. thermocellum* cannot utilize xylose nor hemicellulose.
- The microbe cannot be engineered genetically.




*C. thermocellum* utilizes cellulose (C6), but not hemicellulose (C5 sugars) — **1926 – 2016**

***A Game Changer***

NREL genetically modified strain (***xylAB***) to enable C5 sugar (xylose) co-utilization — **2017 – 2018**

**2018 - 2020** — NREL evolved strains (created strain ***19-9***) for improved growth on monomeric xylose and $H_2$ production rate on **hemicellulose (HC) sugars**

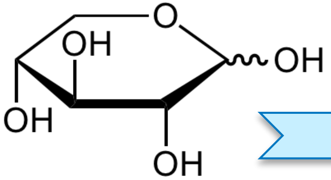
**2020 – 2021**
**Co-utilizing hemi-/cellulose for $H_2$ production** — Enabled the co-utilization of hemi-/cellulose (**BX**)

**Currently working to file a provisional patent**

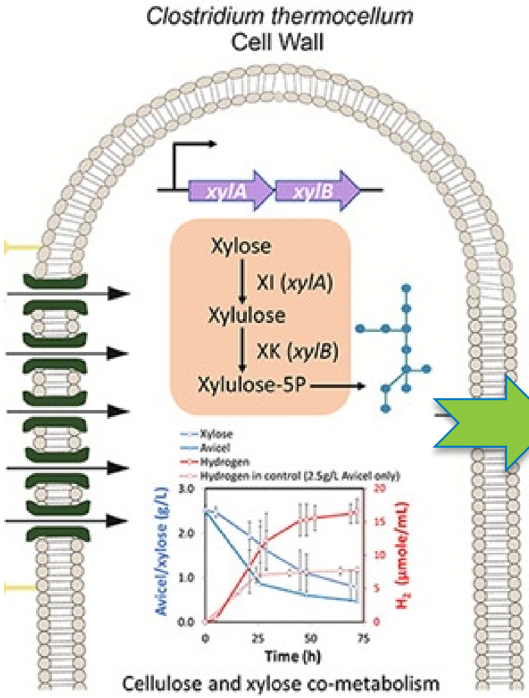
**Cellulose/hemicellulose co-utilization will lower feedstock cost**

# Convert Xylose to $H_2$: a Ground-breaking Achievement!!

***A Really Big Deal!!***




**Xylose**




**BioH$_2$**

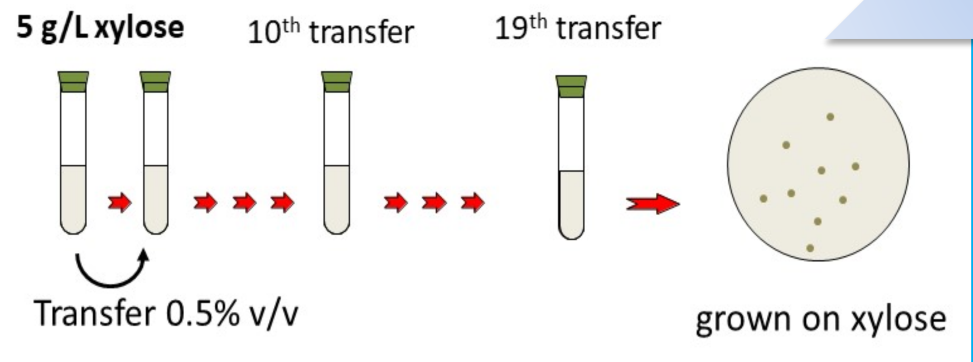
- Enable xylose utilization by adding two foreign genes.
- Double $H_2$ production upon adding equal amounts of xylose and cellulose, vs. cellulose alone.

Wei et al. (2018) *Biotechnol. Bioeng.*

**An achievement 92 years after the first discovery of this microbe, a critical first step toward lowering feedstock cost!**

# Convert *Hemicellulose** to $H_2$

## 1. Adaptive Laboratory Evolution

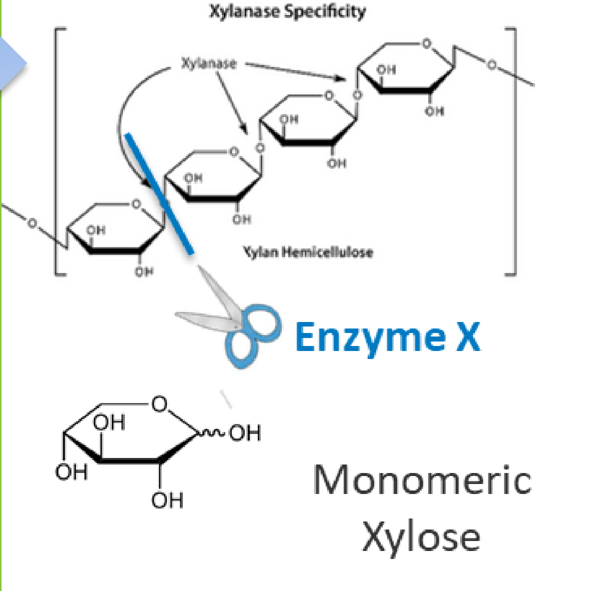



- **Increase total $H_2$ by 67% (to 3.5 $LH_2/L$)**
- **Increase rate of $H_2$ by 24%**

**These achievements led to funding supports from DOE Office of Science.**

***Add Gene X*****

## 2. Gene X Hydrolyzing Hemicellulose to xylose

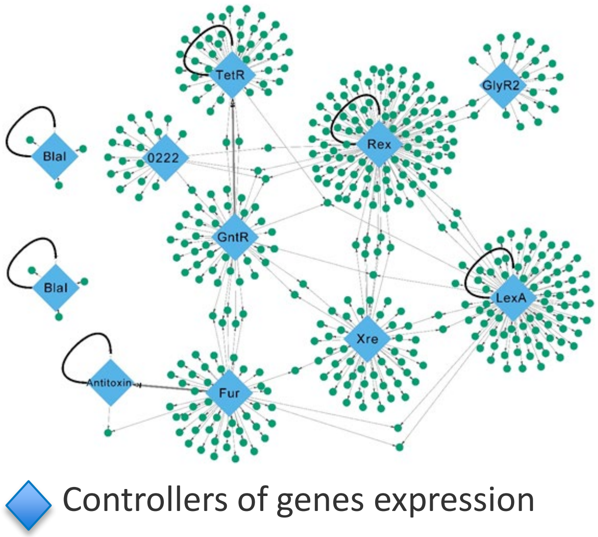



- **Increase total $H_2$ by 95% (to 4.1 $LH_2/L$)**
- **Increase rate of $H_2$ by 39%**

*from pretreated corn stover; **provisional patent underway

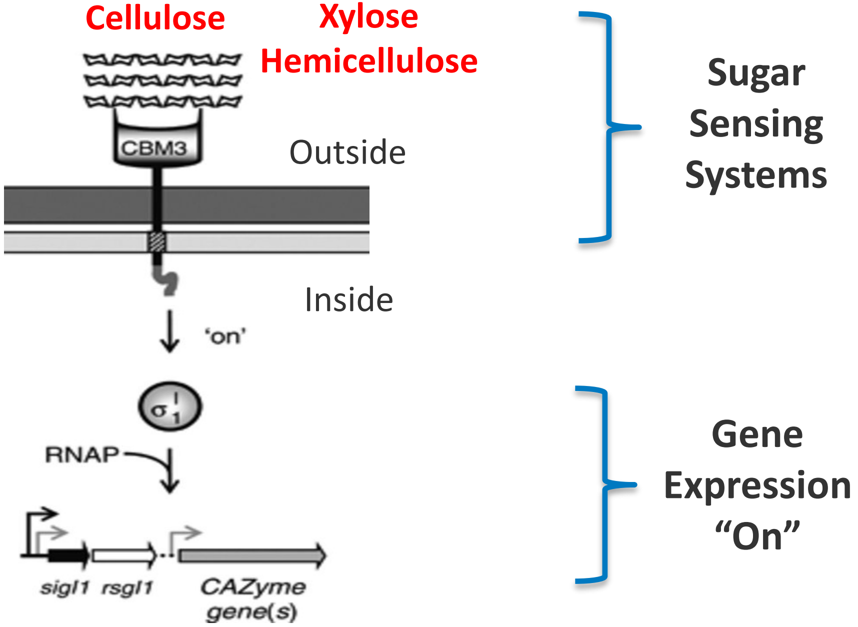
# Cutting-edge Research Drives New Frontiers of Science

Characterize gene regulatory network, which could be rewired to increase $H_2$ yield




Hebdon et al. (2021) *Frontiers in Microbiol.*

Probe how cells sense "food", trigger gene expression, and convert more sugars to $H_2$

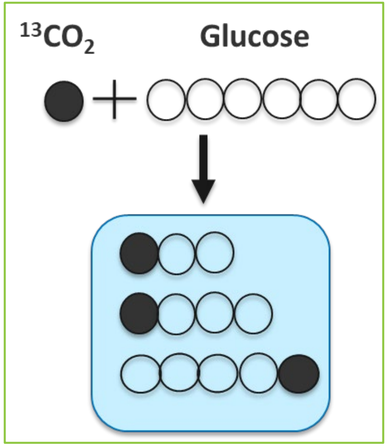



Katherine Chou

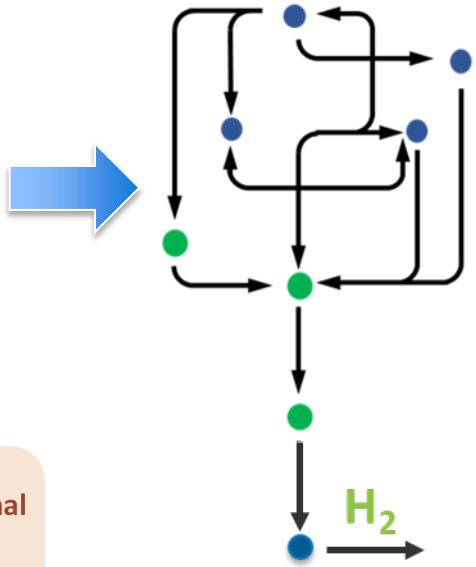
**The knowledge is pivotal to increasing $H_2$ production and collaboration with Oak Ridge National Lab (left) and UCLA (right).**

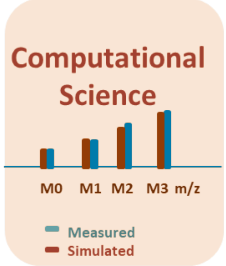
# *A Seminal Discovery: C. thermocellum* Can Fix $CO_2$ While Converting Waste Biomass to $H_2$

- **Tracking Carbons**
- **Machine Learning**




**Carbon Flux Map**

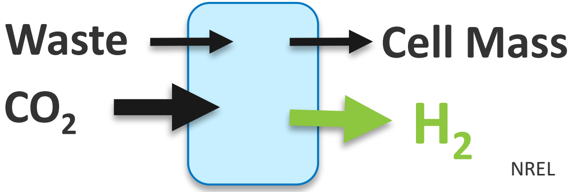



Wei et al. (2016) *Proc. Natl. Acad. Sci.*

- $^{13}C$-carbon tracer is a powerful tool to track the fate and flux of carbon inside the cells
- Flux map analysis revealed $CO_2$ fixation **via a novel pathway,** with ~**15% increase in carbon efficiency.**

**This cross-cutting technology could reduce carbon emission.**



# Summary

- Engineer *C. thermocellum* to use xylose and hemicellulose, the outcomes increase rates and total amounts of $H_2$ and reduce feedstock cost.
- Probing gene regulatory network and sugar sensing will increase $H_2$ production
- Identify a novel $CO_2$-fixation pathway: build cross-cutting science toward carbon capture while producing $H_2$.

# Collaboration

PennState
Bruce Logan

UCLA
James Liao

Berkeley Lab

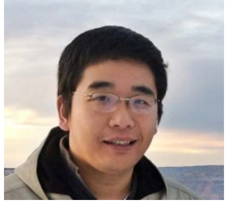
Pacific Northwest National Laboratory

Argonne National Laboratory

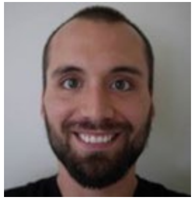
# Acknowledgements

Katherine Chou
Principal Investigator

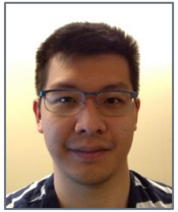
Lauren Magnusson



Wei Xiong



Trevor Croft



Jonathan Lo

Luis H. Reyes

Skyler Hebdon

DOE HFTO and NREL LDRD for funding support

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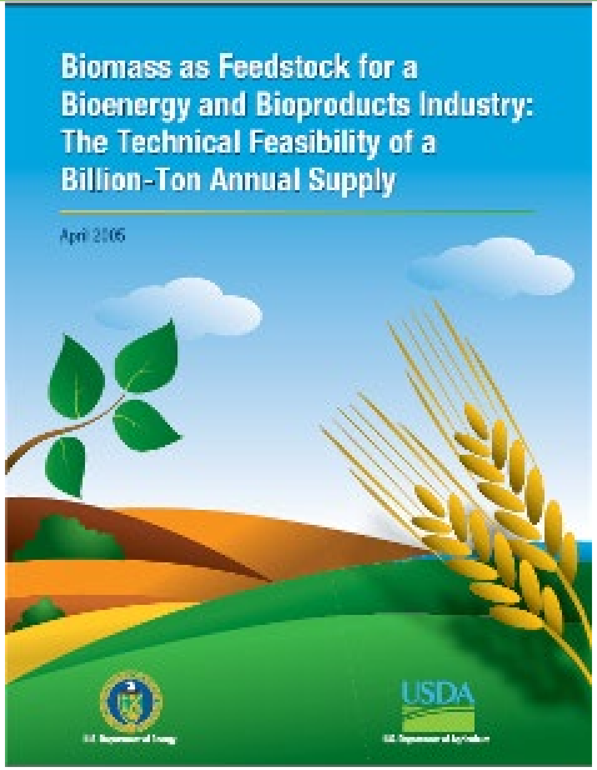
# Biohydrogen Production using Microbial Electrolysis Cells

Bruce E. Logan, Penn State University

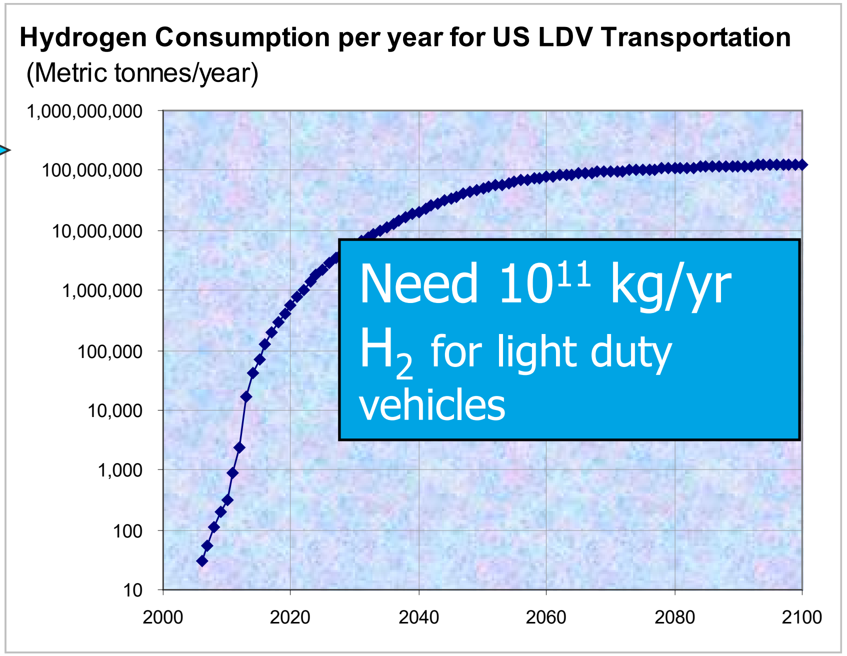
Hydrogen Shot Summit

# Cellulose to $H_2$: Getting past the fermentation barrier



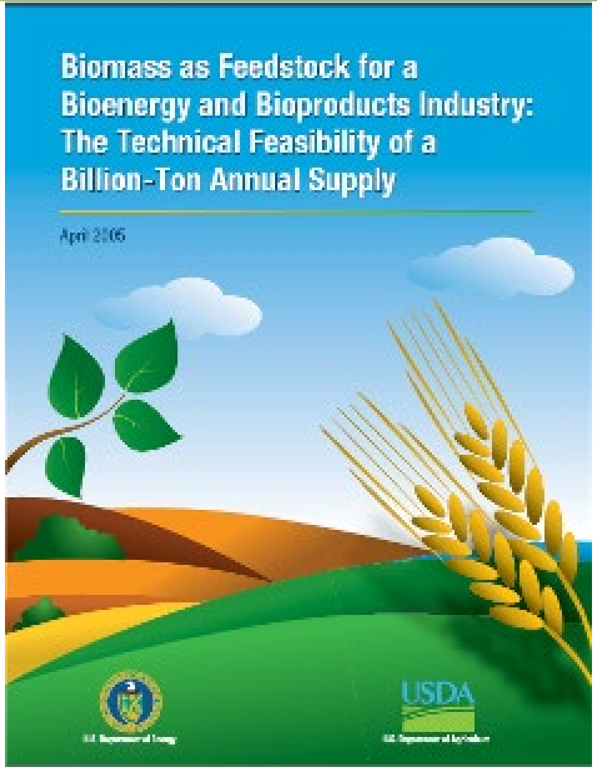

**In Theory: Cellulose → 12 $H_2$**

1.34/2 billion ton/y of cellulose could produce ~$10^{11}$ kg/yr $H_2$




Need $10^{11}$ kg/yr $H_2$ for light duty vehicles

# Cellulose to $H_2$: Getting past the fermentation barrier

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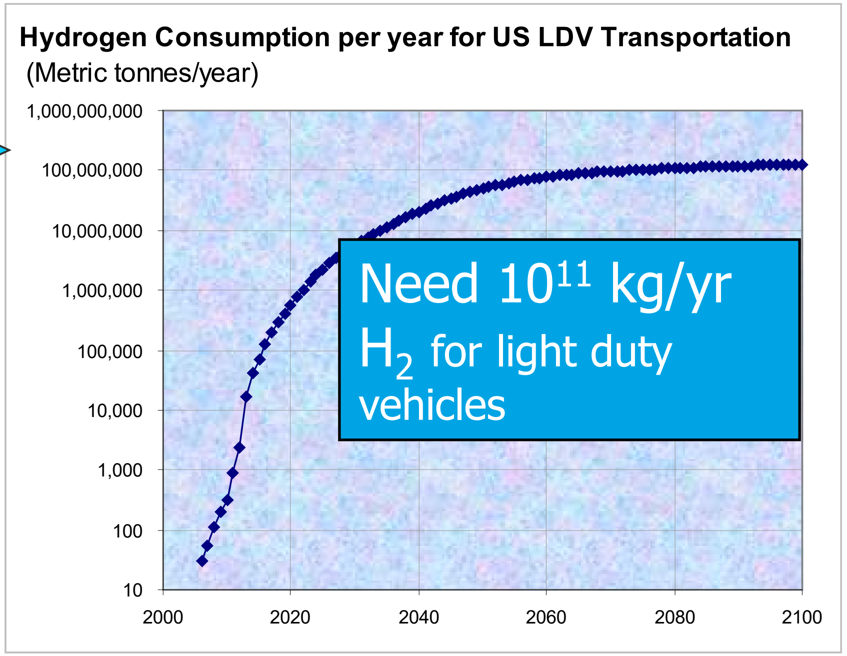



The cellulose/biomass "fermentation barrier"

Cellulose; Wastewaters; *Any biodegradable organic matter*

**Fermentation**

$$C_6H_{12}O_6 + 2\ H_2O \rightarrow 4\ H_2 + 2\ C_2H_4O_2 + 2\ CO_2$$

Achieves ≤ 4 $H_2$ (+ 2 Acetate)

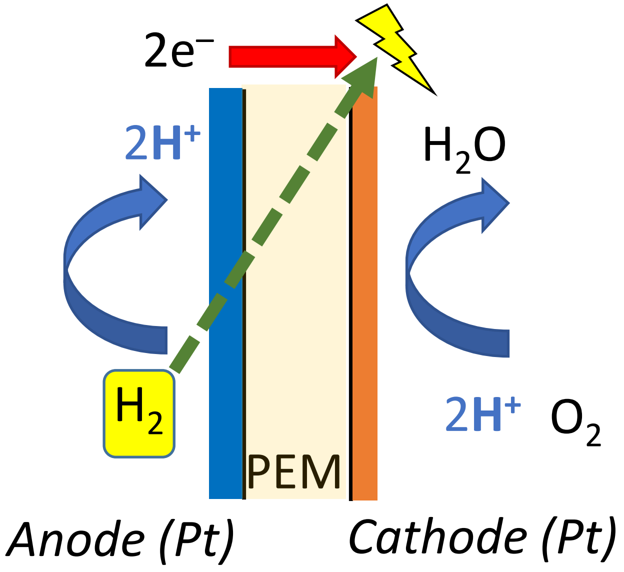
**Microbial Electrolysis Cells (MECs)**

$$2\ C_2H_4O_2 + 2\ H_2O \rightarrow 8\ H_2 + 4\ CO_2$$

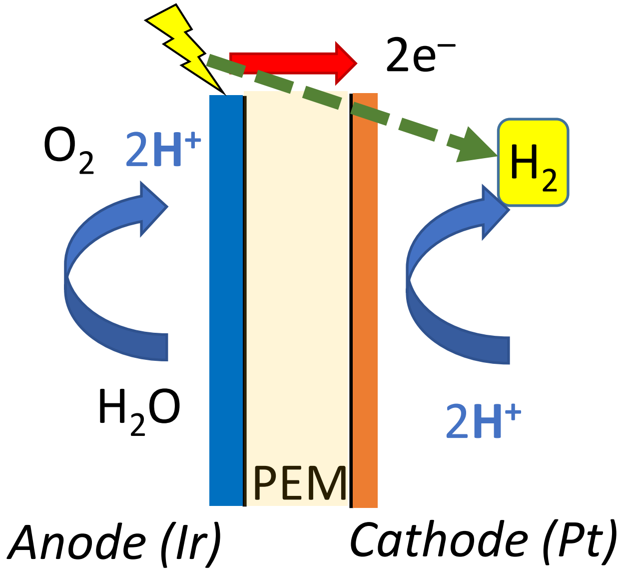
Achieves ≤ 8$H_2$ → total possible = 12$H_2$

# Fuel cells versus (PEM) water electrolyzers

**Fuel Cell:**
Produces electricity using $H_2$ (+ $O_2$)




**Water Electrolyzer:**
Produces $H_2$ using electricity

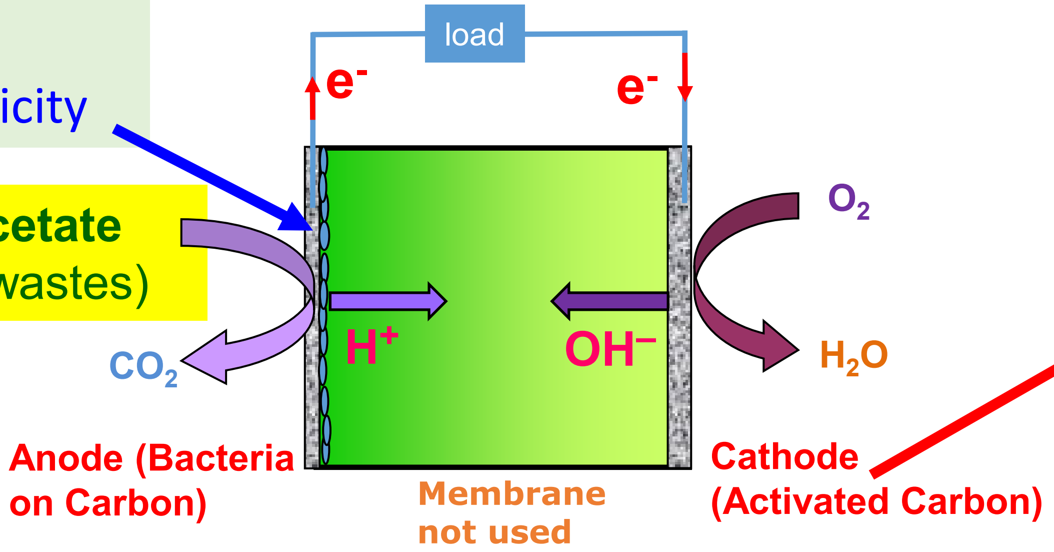


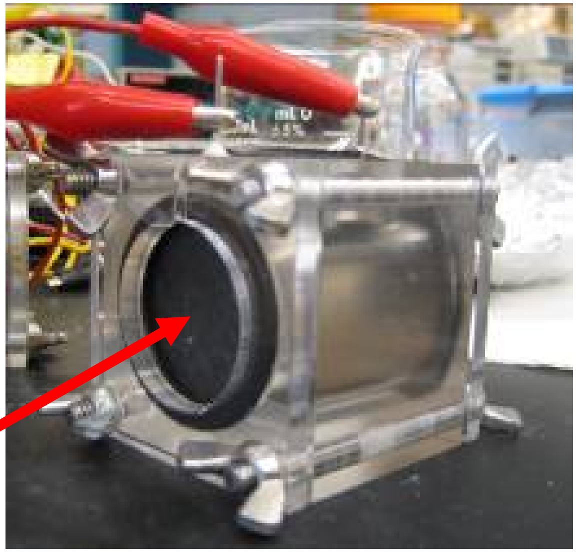
# Microbial Fuel Cells (MFCs) make electricity using microorganisms

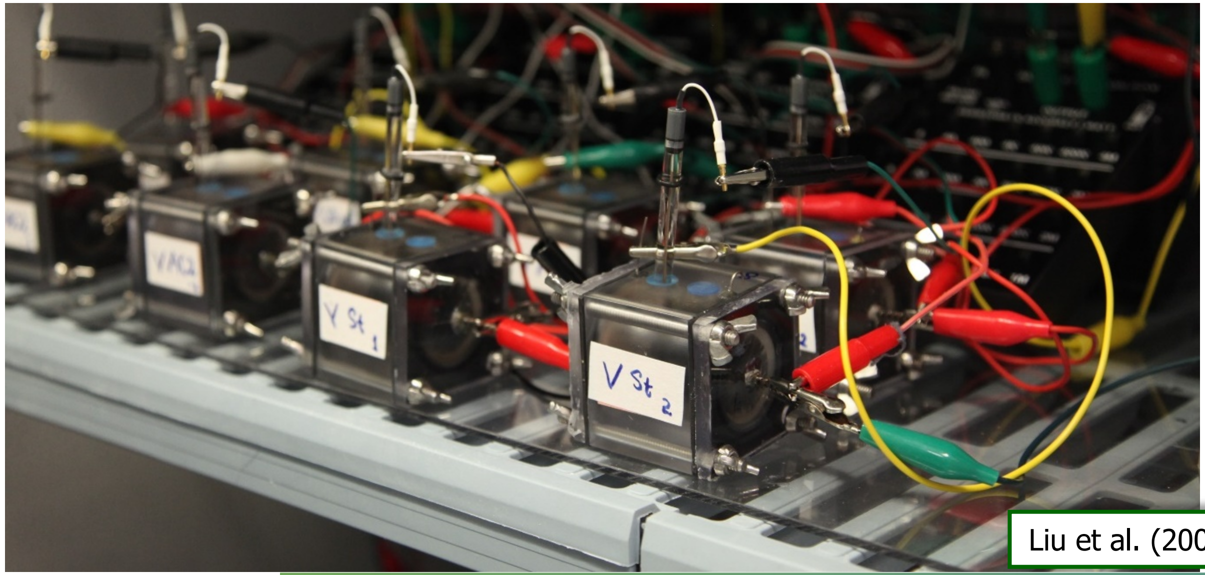
## MFCs

Bacteria that produce electricity

**Fuel = Acetate**
(+organic wastes)



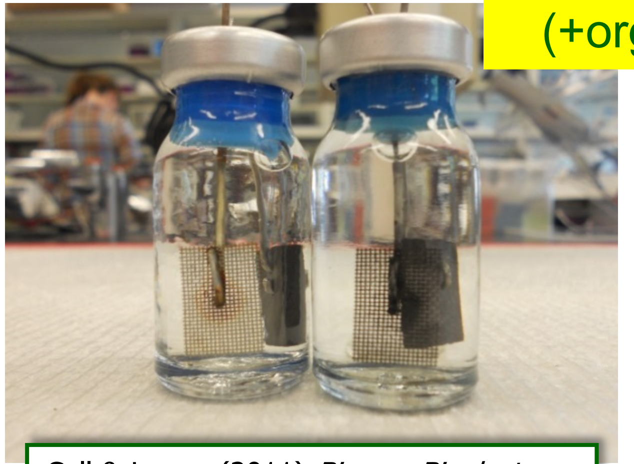





Liu et al. (2004) *Environ. Sci. Technol.*

# Microbial Electrolysis Cells (MECs) produce $H_2$

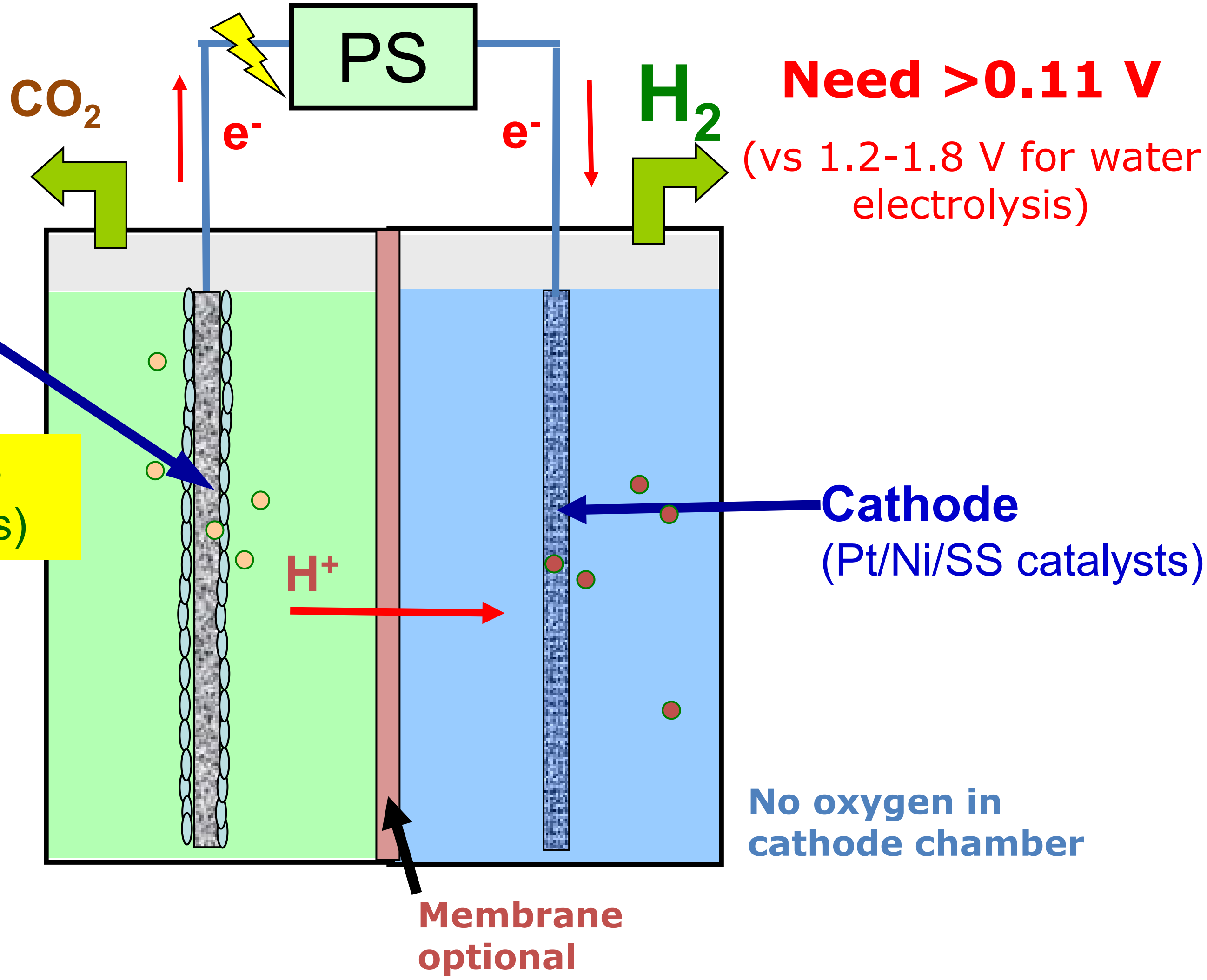
## MECs



Call & Logan (2011) *Biosen. Bioelectron.*

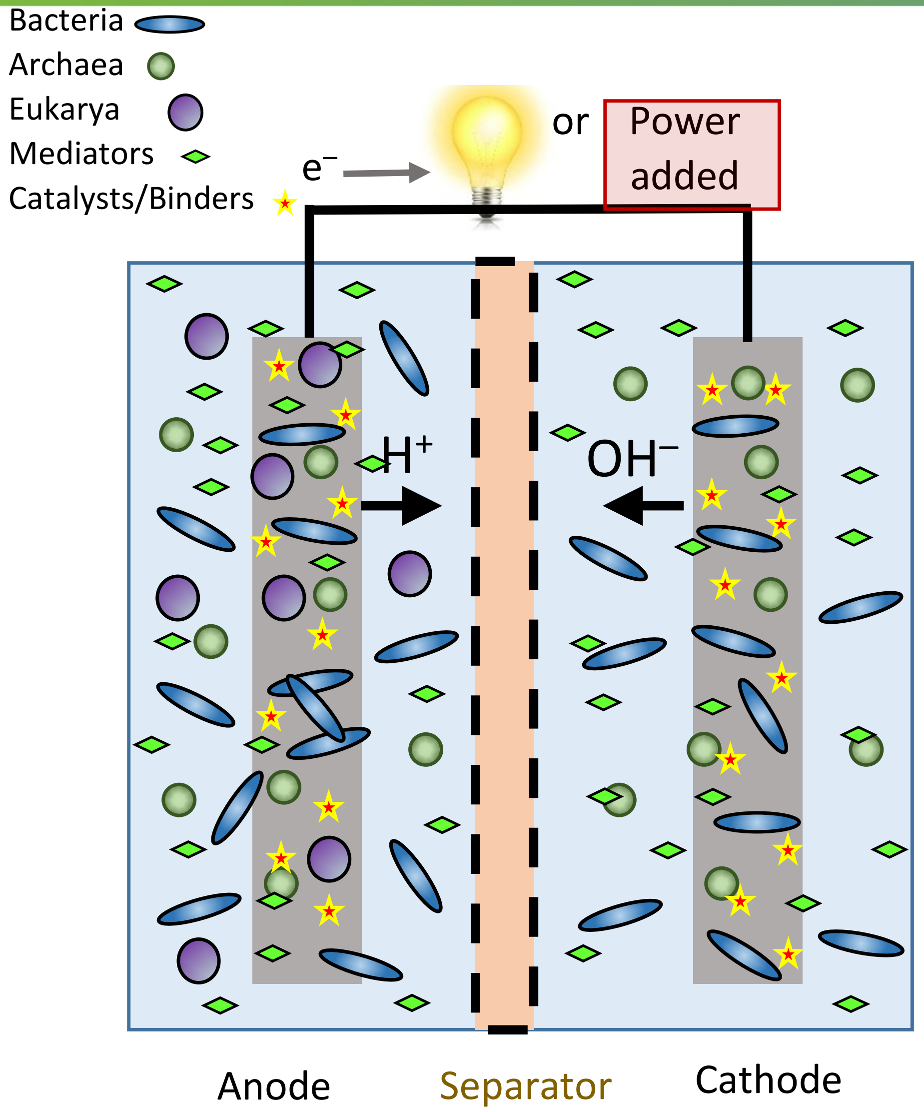
**Fuel = Acetate**
(+organic wastes)

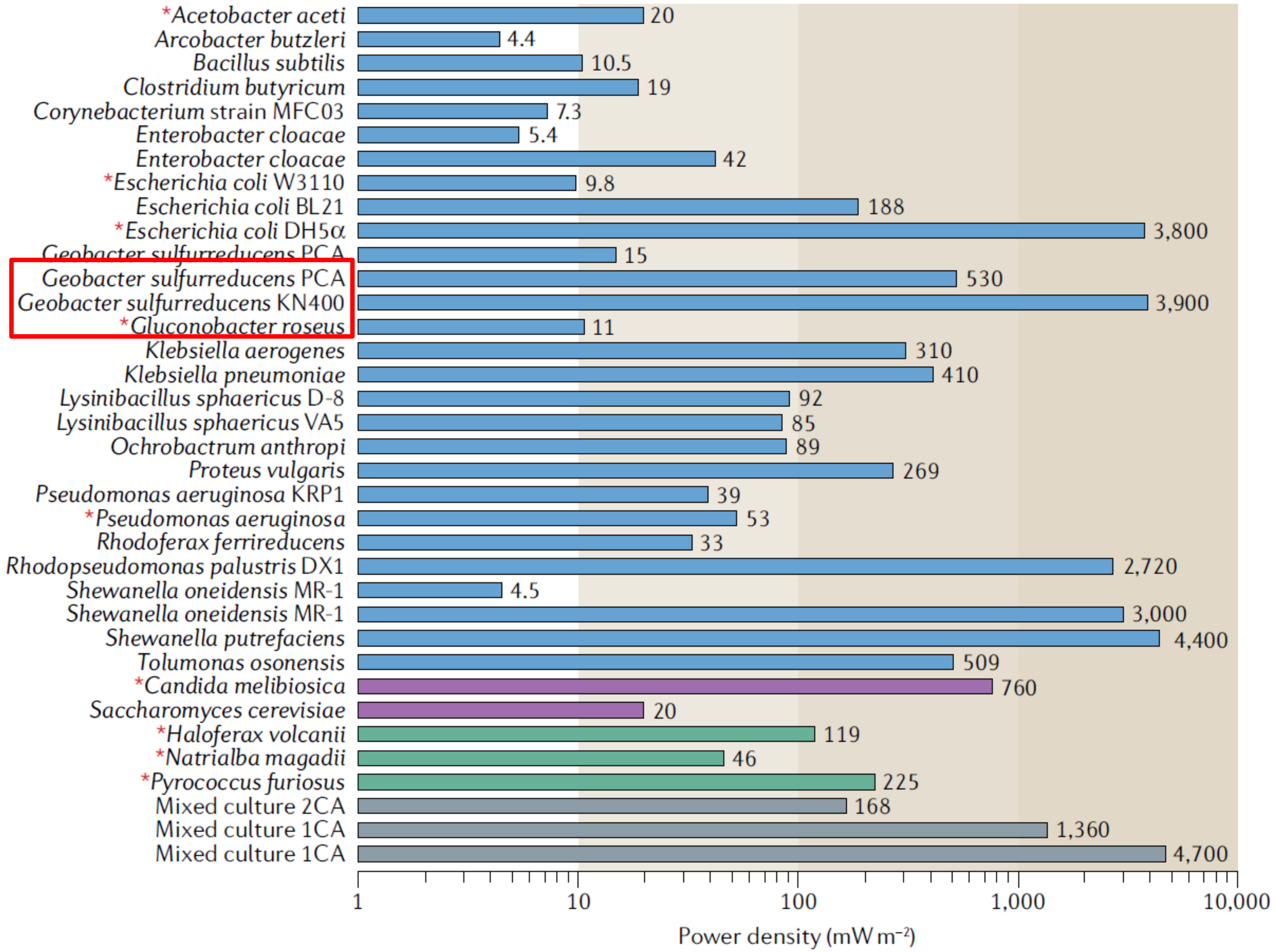
**Bacteria (bioanode)**




Liu, Grot & Logan (2008) *Environ. Sci. Technol.*

# What microorganisms produce current = exoelectrogenic?



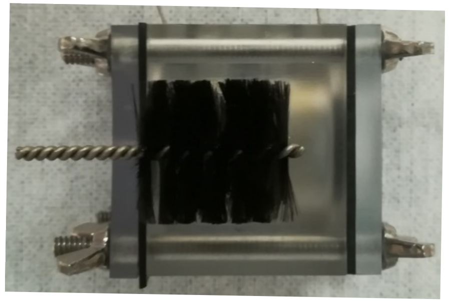




Logan, Rossi, Ragab, Saikaly (2019) *Nature Rev. Microbiol.*

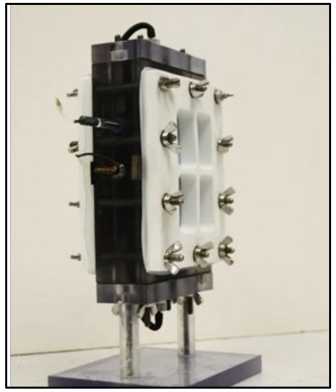
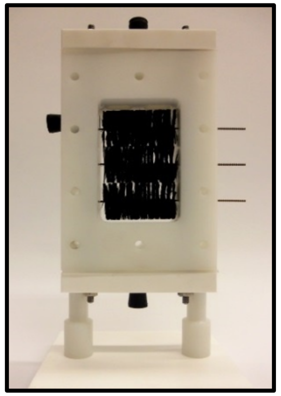
# Scaling up MFCs: from laboratory to pilot scale

MFCs

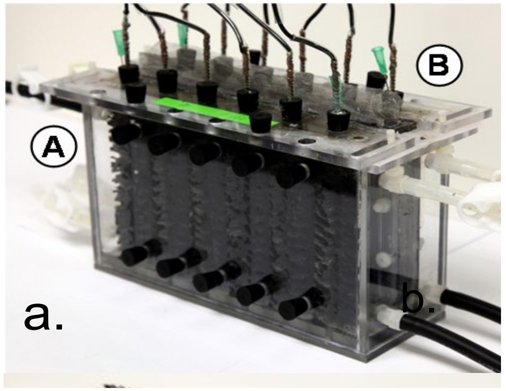
**Gen 0**: 0.025 L, 25 $m^2/m^3$

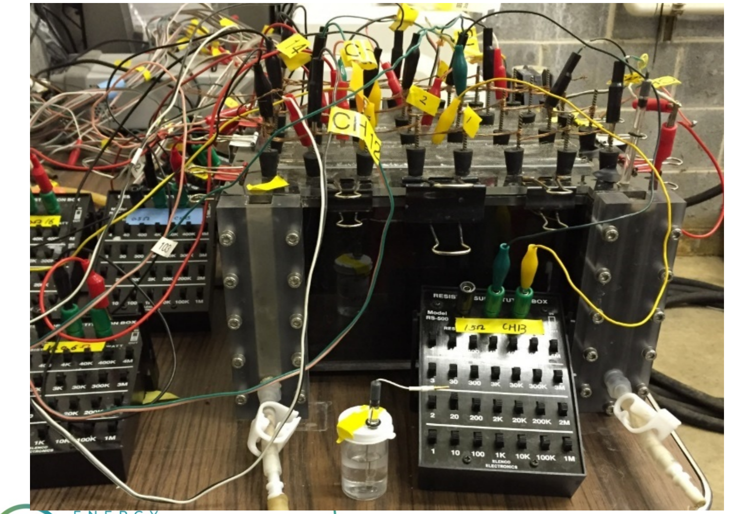
**Gen 1**: 0.13 L, 25 $m^2/m^3$

**Gen 2**: 2 L, 20 $m^2/m^3$

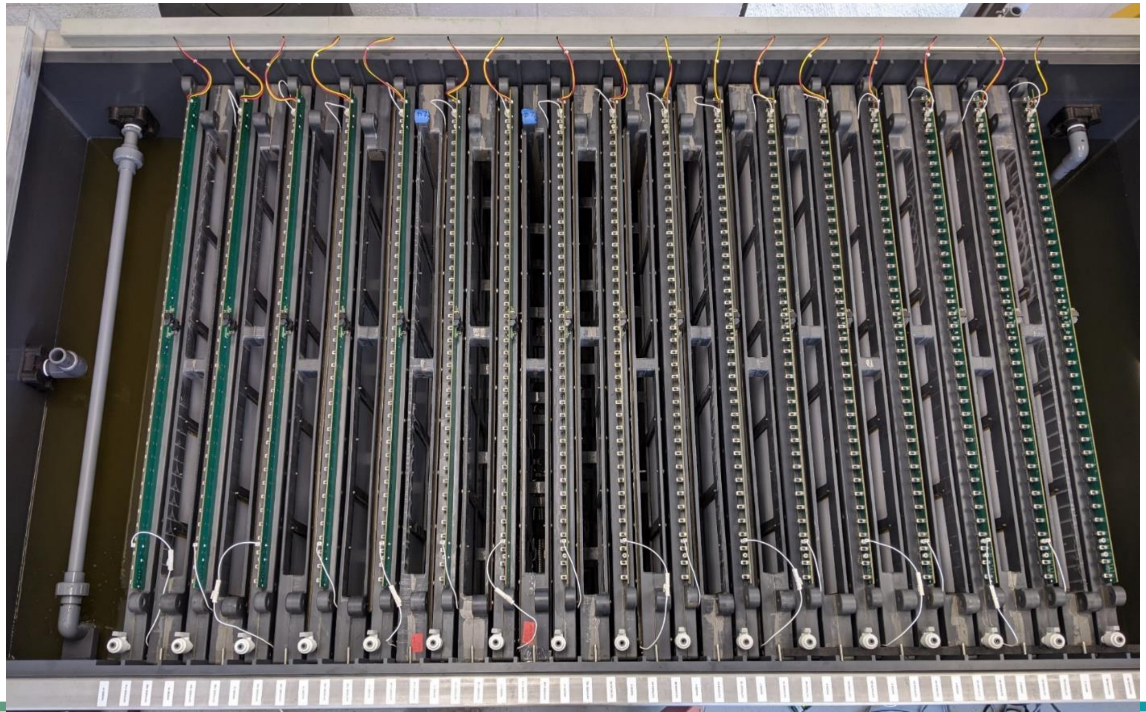



**Gen 3**: 6.1 L, 20 $m^2/m^3$



**Pilot-Scale MFC:**

850 L active volume, 25 $m^2/m^3$

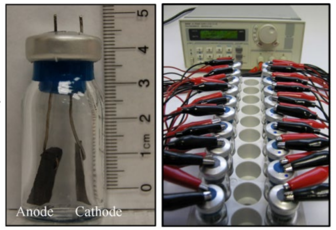


# Scaling up MECs: from laboratory to pilot scale: Part I

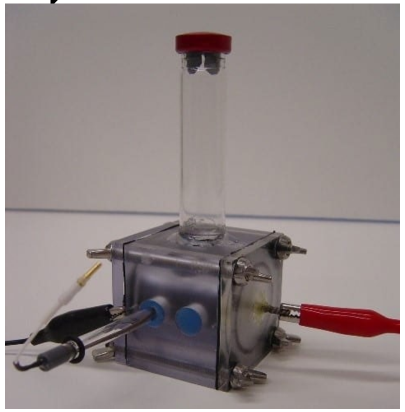
## MECs

**Single-Chamber MECs: $H_2 \rightarrow CH_4$**

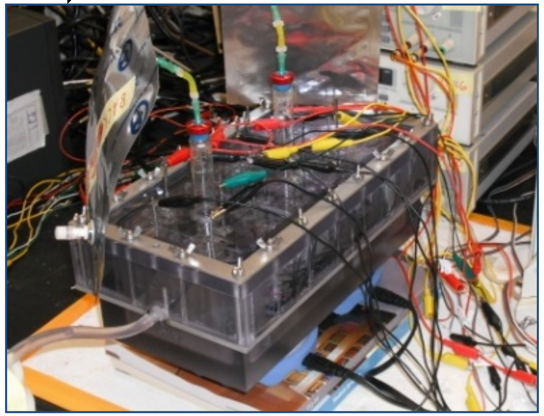
**5 mL mini-MEC**




**28 mL MEC**

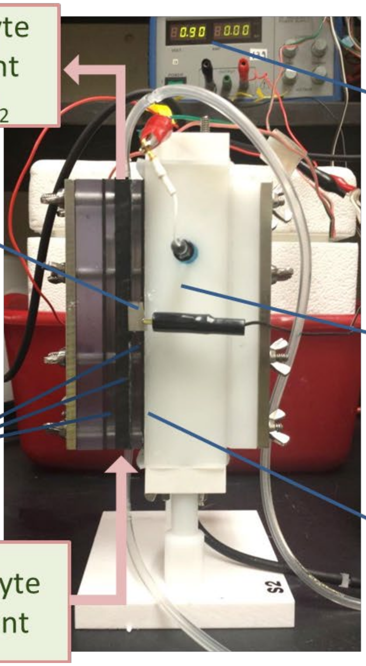


**2.5 L MEC**



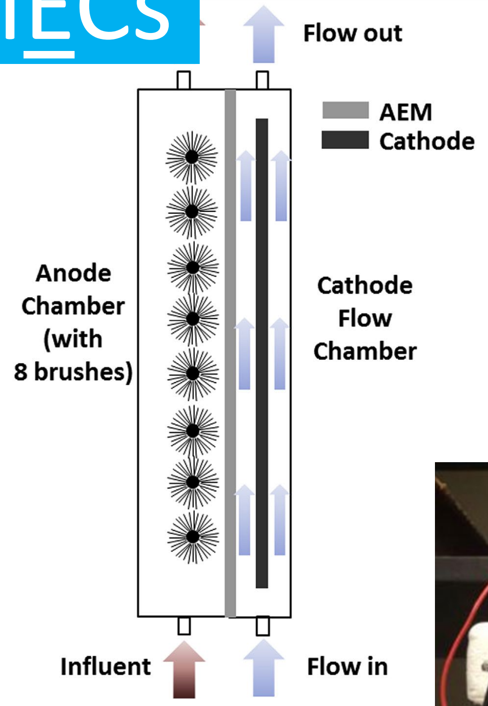
**1000 L MEC** X

**Two-Chamber MECs: $H_2$ recovery**

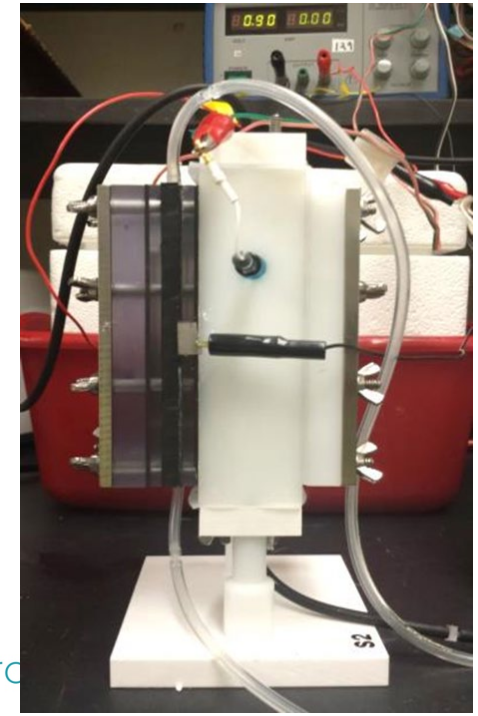


# Scaling up MECs: Part II, capturing $H_2$

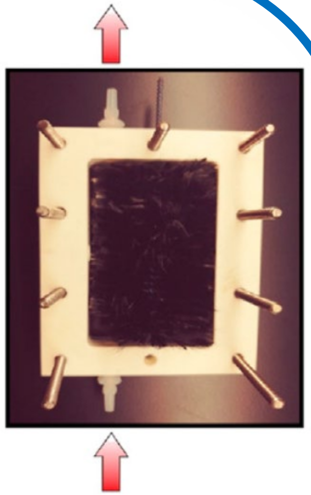
MECs

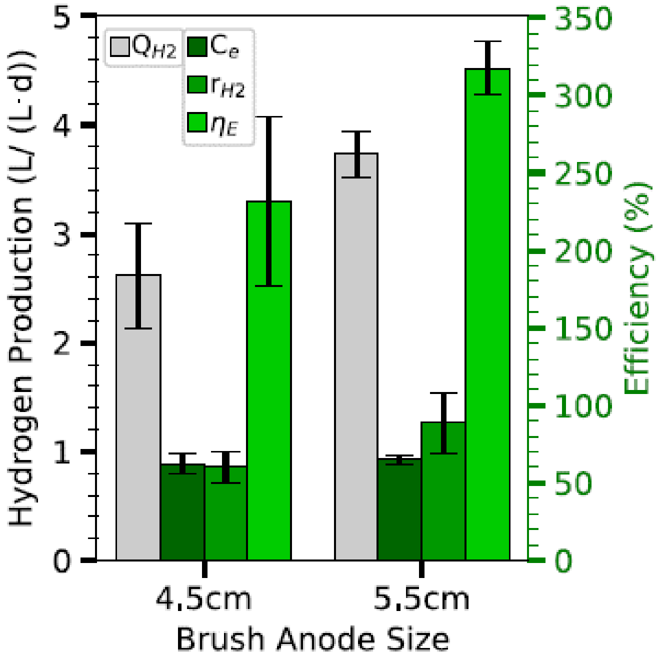



- Flow by brushes
  + SS cathode
  - 60 A/m$^3$
  - 1.3 L/L-d



- Flow through brushes
  + SS wool cathode
  - 200 – 400 A/m$^3$
  - 2.6 – 5.2 A/m$^2$
  - 3.8 L/L-d

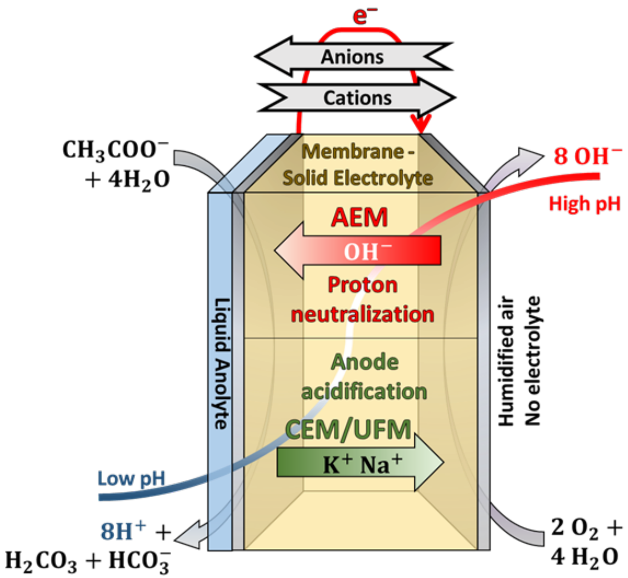




# Scaling up MECs Part III: Increasing current and $H_2$ production rates

**MFCs** — Applying lessons learned from MFCs to MECs — **MECs**

**Applying Design features of our best MFCs → MECs**



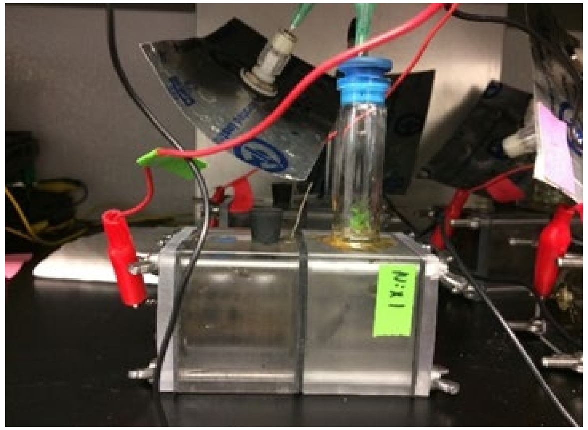

Ultra-compact **MFC** design increased current densities from 8 to 50 A/m²

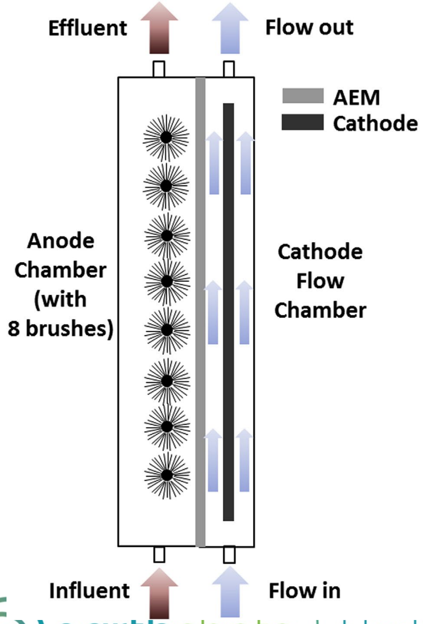
Rossi, Wang, Logan (2019) J. Power Sources

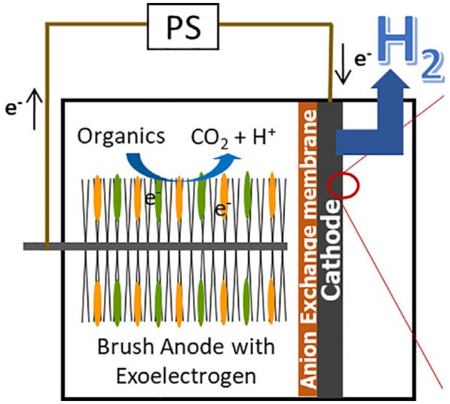
- Improved **MECs** (in progress)
  - Avoided solution resistance by using a solid electrolyte anion exchange membrane (AEM) with gas phase electrolyte
  - Unique AEM design reduced anode and cathode resistances by balancing pH
- *Preliminary MEC results*: 17x increase in performance
  - 42 A/m²-d (versus 5 A/m²)
  - 63 L/L-d (versus ~3.8 L/L-d)
  - Highest $H_2$ production rate achieved under these solution conditions

# Avoiding the use of precious metals in MECs

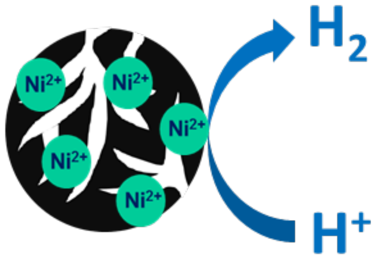
Stainless Steel wool cathodes

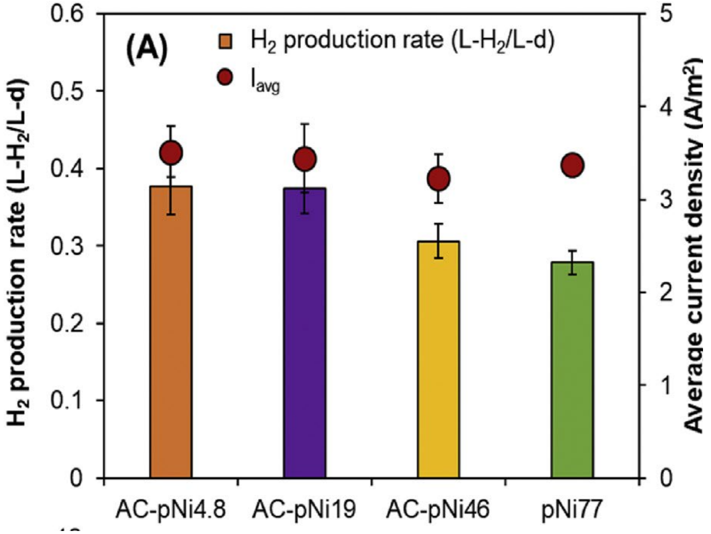




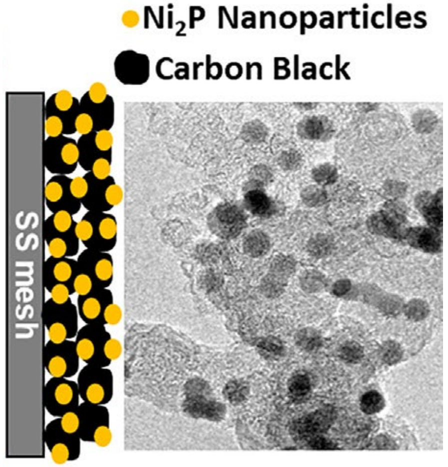



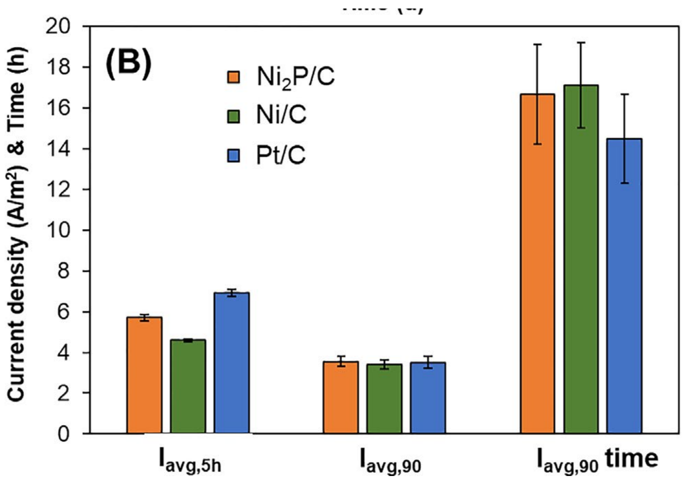

Nickel particles, pNi on activated carbon




Nickel Phosphide $Ni_2P$



# Why use biomass (electrolyzers) to achieve $1H$_2$/kg?

- **Water electrolyzers** require 2 steps
  - Water purification (reverse osmosis + deionization)
  - Electrolyzer operation using electrical power
- Electricity use is high
  - Minimum of electrical energy for water splitting is 33 kWh/kg $H_2$ (thermodynamics)
- $1 kg $H_2$ requires for electricity:
  - $0.03/kWh for electricity (thermodynamic limit)
  - $0.02/kWh considering current efficiencies (70%)
- Precious metals may be required.
  - PEM uses Ir, Pt; AEM does not (Ni-based)
- Small, compact reactors, high electricity demand

- **Biomass** (with electrolyzers) requires 2 steps
  - Biomass fermentation
    - Fermentation is spontaneous, so no energy input needed during process (neglecting reactor stirring, pumps)
    - Produces 4 moles H2 per cellulose (of maximum = 12)
  - Microbial electrolysis Cells (MECs)
    - Minimum electrical energy is only $1/10^{th}$ electrical energy compared to water electrolyzers
- $1 kg $H_2$ requires for electricity
  - $0.30/kWh for electricity (thermodynamic limit) for 8/12 moles of $H_2$
  - $0.45/kWh for 12/12 moles of H2.
- Precious metals not required.
- Large reactors used, need transport of biomass, low electricity demand

# CONCLUSIONS

- MECs use bacteria as the "catalyst" to produce an electrical current,
  - Fuel = waste organic matter
  - $H_2$ produced electrochemically (as in a water electrolyzer) using biomass electrons
- MEC designs have lagged those of MFCs… but innovations can improve both systems
- Recent MEC designs achieved 63 L/L-d, with 100 L/L-d on the horizon without using precious metals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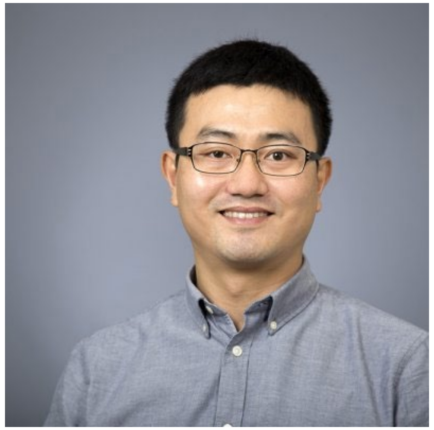
Recent work on high-performance MFCs and MECs



**Dr. Kyoung-Yeol Kim**
**Assistant Professor (SUNY Albany)**
Two-chamber brush MECs and HER catalysts

# QUESTIONS?